PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-082510

(43)Date of publication of application : 28.03.1995

(51)Int.Cl. C09D 5/00
C09D 7/12
G02B 1/11

(21)Application number : 05-186984

(22)Date of filing : 30.06.1993

(71)Applicant : HOYA CORP

(72)Inventor : MATSUMOTO KENJI
TAKAWA HIROYUKI
KATO YASUKO

(54) COATING MATERIAL FOR PREVENTING OF INTERNAL REFLECTION IN OPTICAL MEMBER AND OPTICAL MEMBER

(57)Abstract:

PURPOSE: To obtain a coating material which gives a film on an optical member for the prevention of internal reflection with little total reflection at the interface between them and has sufficient resistance to isopropyl alcohol used for cleaning an optical member and an optical member having a film for the prevention of internal reflection.

CONSTITUTION: The coating material contains fine black inorganic partition having a diameter of at most 0.1μm and a refractive index of at least 1.5, or fine nonblack inorganic particle having a diameter of at most 0.1μm and a refractive index of at least 1.5 and a black pigment. The optical member has a film for the prevention of internal reflection which contains the above black or nonblack particles and a black pigment and which has a refractive index different by at most 0.1 from that of the optical member.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other

07-082570

* NOTICES *

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

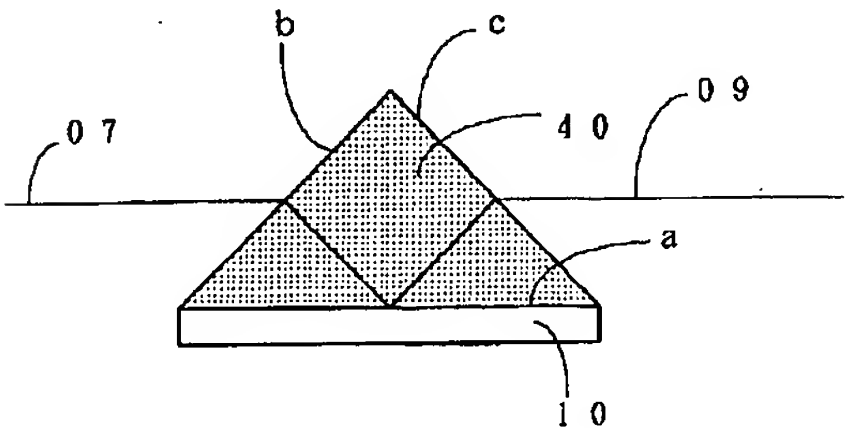
CLAIMS

[Claim(s)]
[Claim 1] The paint for internal reflection prevention of the optical faculty material characterized by containing the black non-subtlety particle whose refractive index a particle diameter is 0.1 micrometers or less, and is 1.5 or more.
[Claim 2] The paint according to claim 1 whose refractive index of a black non-subtlety particle is 1.7 or more.
[Claim 3] The paint according to claim 1 or 2 which the amount from which a difference with the refractive index of the optical faculty material by which a black non-subtlety particle is applied to the aforementioned paint into a paint becomes 0.1 or less was made to contain.
[Claim 4] The paint for internal reflection prevention of the optical faculty material characterized by containing the un-black non-subtlety particle whose refractive index a particle diameter is 0.1 micrometers or less, and is 1.5 or more, and black pigment.
[Claim 5] The paint according to claim 4 whose refractive index of an un-black non-subtlety particle is 1.7 or more.
[Claim 6] The paint according to claim 4 or 5 which the amount from which a difference with the refractive index of the optical faculty material by which an un-black non-subtlety particle is applied to this paint into a paint becomes 0.1 or less was made to contain.
[Claim 7] The paint of the claim 4-6 which made black pigment contain in a paint so that the optical density of this paint may become one or more given in any 1 term.
[Claim 8] It is the optical faculty material which has an internal reflection prevention film, and the particle diameter of the aforementioned internal reflection prevention film is 0.1 micrometers or less. And the black non-subtlety particle whose refractive index is 1.5 or more is contained, or a particle diameter is 0.1 micrometers or less. and the un-black non-subtlety particle and black pigment whose refractive index is 1.5 or more -- containing -- and the refractive index of the aforementioned internal reflection prevention film -- the aforementioned optics -- the optics characterized by being the refractive index of a member, and 0.1 or less difference -- a member

---

[Translation done.]

Drawing selection [Representative drawing]



[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to the optical member which has the internal reflection prevention film formed using the paint for internal reflection prevention of optical faculty material, and this paint for internal reflection prevention. In more detail, this invention relates to the optical member which has the paint for internal reflection prevention and internal reflection prevention film which are applied to the side which does not penetrate the light of optical faculty material in order to prevent generating of the flare of optical faculty material, such as a lens and prism, a ghost, etc.
[0002]
[Description of the Prior Art] The incident light to an optical member carries out internal reflection of the optical members generally used for optical instruments, such as a camera and a microscope, such as a lens and prism, according to the optical faculty material side, they generate the flare, a ghost, etc., and the optical property of an optical instrument is reduced. In order to prevent this internal reflection, applying the black paint for internal reflection prevention to the optical faculty material side, and forming an internal reflection prevention film is known. Generally the black paint which distributed carbon black to the vehicle is used for this black paint for internal reflection prevention.
[0003] Drawing 1 is explanatory drawing about the internal reflection of optical faculty material. In drawing 1 , the incident light 01 to the optical faculty material 20 turns into the total reflection light 03 and refracted light 05 in an interface with the internal reflection prevention film 10, and the refracted light 05 is absorbed by the black internal reflection prevention film 10.
[0004] When the refractive index of optical faculty material is about 1.5, the black paint for internal reflection prevention which used the above carbon black can prevent internal reflection effectively. However, if the refractive index of optical faculty material becomes high or more with 1.7, the internal reflection prevention effect will fall remarkably. This is for the refractive-index difference of an internal reflection prevention film and an optical member to become large, and for the total reflection in the interface of an internal reflection prevention film and an optical member to increase.
[0005]
[Problem(s) to be Solved by the Invention] In recent years, the refractive index of a great portion of material used as an optical member is in the range of 1.45 to 1.85. Moreover, for some uses, 1.85 or more optical members are also used for the refractive index. Many of vehicles used for the paint for internal reflection prevention have a refractive index in the range of 1.45 to 1.60 to it. Consequently, in such black paints using the vehicle of a low refractive index, internal reflection of the optical faculty material of a high refractive index was not able to be prevented comparatively effectively. That is, in the black paints which used carbon black as the main pigment, the refractive index of carbon black has not decreased the total reflection light in the interface of an internal reflection prevention film and an optical member low.
[0006] Then, the paint for internal reflection prevention usable to a high refractive-index optical member is proposed. For example, to JP,57-8264,A, the paint for internal reflection prevention which mixed

metallic oxides, such as a tri-iron tetraoxide, an iron sesquioxide, and manganese dioxide, to the vehicle which consists of styrene-ized melamine resin and acrylic resin is indicated. Black metallic oxides, such as a tri-iron tetraoxide used here, an iron sesquioxide, and manganese dioxide, have a comparatively high refractive index.

[0007] However, total reflection in the interface of the internal reflection prevention film and optical member which were formed using this paint was not able to be effectively decreased only by making the refractive index of a black metallic oxide high like the paint for internal reflection prevention of a publication to JP,57-8264,A. This is based on the following reasons. the light which will turn into total reflection light if the total reflection in the interface of an internal reflection prevention film and an optical member is examined in detail -- once -- the paint layer for internal reflection prevention -- leaking -- taking out (exudation) -- again -- optics -- a member -- it returns to inside and becomes total reflection light this -- it begins to leak and the depth of light is about 1 / four waves It is effective in this ** that begins to leak and lessens the refractive-index difference of the refractive index of an internal reflection prevention film and optical faculty material in the depth of light lessening total reflection light.

[0008] However, by the internal reflection prevention film given in JP,57-8264,A, it begins to leak, and to the depth of light, since the particle diameter of a black metallic oxide was too large, total reflection in the interface of an internal reflection prevention film and an optical member was not able to be decreased. This state is typically shown in drawing 2 . In drawing 2 , the metallic-oxide particle 30 is large to exudation depth m, and a metallic oxide 30 does not exist effectively in the field of exudation depth m. For this reason, in the field of exudation depth m of the interface of an internal reflection prevention film and an optical member, since a vehicle exists mostly, total reflection light in the interface of an internal reflection prevention film and an optical member cannot be decreased.

[0009] The paint for internal reflection prevention which mixed and paint-ized the coal tar in the JP,55-34837,B official report at the vehicle which consists of a polymer of the heavy-metal salt of unsaturated fatty acid is indicated to it. This paint for internal reflection prevention begins to leak, and its refractive index is high in the depth of light, and it is effective in preventing total reflection. However, since the coal tar was used, the adhesion of optical faculty material is inadequate, and it dissolved in organic solvents, such as isopropyl alcohol used for washing of optical faculty material, and there was a problem that the duty as an internal reflection prevention film was unmaintainable.

[0010] Then, the purpose of this invention has little total reflection in the interface of an internal reflection prevention film and an optical member, and it is to offer the paint for internal reflection prevention which can form the internal reflection prevention film which has resistance of enough also in organic solvents, such as isopropyl alcohol used for washing of optical faculty material.

[0011] Furthermore, this invention has little total reflection in the interface of an internal reflection prevention film and an optical member, and it is to offer the optical member which has the internal reflection prevention film which has resistance of enough also in organic solvents, such as isopropyl alcohol used for washing of optical faculty material.

[0012]

[Means for Solving the Problem] this invention relates to the paint for internal reflection prevention of the optical faculty material characterized by containing the black non-subtlety particle whose refractive index a particle diameter is 0.1 micrometers or less, and is 1.5 or more.

[0013] Furthermore, this invention relates to the paint for internal reflection prevention of the optical faculty material characterized by containing the un-black non-subtlety particle whose refractive index a particle diameter is 0.1 micrometers or less, and is 1.5 or more, and black pigment.

[0014] Moreover, this invention is optical faculty material which has an internal reflection prevention film, and the particle diameter of the aforementioned internal reflection prevention film is 0.1 micrometers or less. And the black non-subtlety particle whose refractive index is 1.5 or more is contained, or a particle diameter is 0.1 micrometers or less. and the un-black non-subtlety particle and black pigment whose refractive index is 1.5 or more -- containing -- and the refractive index of the aforementioned internal reflection prevention film -- the aforementioned optics -- it is related with the

optical member characterized by being the refractive index of a member, and 0.1 or less difference
[0015] The paint of the 1st mode of this invention contains the black non-subtlety particle whose refractive index a particle diameter is 0.1 micrometers or less, and is 1.5 or more. Moreover, the paint of the 2nd mode of this invention contains the un-black non-subtlety particle whose refractive index a particle diameter is 0.1 micrometers or less, and is 1.5 or more. The reason the particle diameter of the non-subtlety particle used by this invention is 0.1 micrometers or less is as follows. The 700nm light begins to leak from the wavelength of 400nm, and the depth of light is about 0.1 to 0.18 micrometers. This invention persons found out that the total reflection in the interface of an internal reflection prevention film and an optical member could be decreased by using this non-subtlety particle that begins to leak and has a particle diameter below the depth of light. In addition, there is especially no limit in the minimum of the particle diameter of a non-subtlety particle. However, the minimum of the particle diameter of a non-[from a practical viewpoint] subtlety particle is about 0.01 micrometers.
[0016] Furthermore, in this invention, a refractive index uses 1.9 or more non-subtlety particles of a high refractive index more preferably 1.7 or more 1.5 or more. Since a non-subtlety particle has resistance of enough in organic solvents, such as isopropyl alcohol, the internal reflection prevention film formed using the paint of this invention has resistance of enough also in organic solvents, such as isopropyl alcohol used for washing of optical faculty material.
[0017] As a black non-subtlety particle which is 1.5 or more, a refractive index can mention a metal nickel particle (refractive index 3.3), a metal iron particle (refractive index 3.2), carbonization silicon (refractive index 2.65), a silicon nitride (refractive index 2.2), and titanium black (before or after a refractive index 2.7), for example. Moreover, two or more sorts of mixture of these non-subtlety particles can also be used. Since especially titanium black has a refractive index as high as 2.7 order and is the black of titanium black, its total reflection in the interface of an internal reflection prevention film and an optical member decreases extremely, and the outstanding paint for internal reflection prevention is obtained.
[0017] As an un-black non-subtlety particle whose refractive index is 1.5 or more For example, a barium-sulfate particle (refractive indexes 1.62-1.64), a barium-carbonate particle (refractive indexes 1.53-1.67), A calcium-carbonate particle (refractive indexes 1.51-1.64), an aluminum-hydroxide particle (refractive indexes 1.51-1.56), Clay (refractive index 1.56), PARIUMU yellow (BaCrO4, refractive indexes 1.62-1.64), An aluminum-oxide particle (refractive index 1.76), a zinc-oxide particle (refractive index 2.0) titanium oxide particle (refractive indexes 2.5-2.9), A zinc sulfide particle (refractive index 2.37), a lead-titanate particle (refractive index 2.7), A zirconium-oxide particle (refractive index 2.4), a red ocher particle (refractive indexes 2.78-3.01), A cadmium-sulfide particle (refractive indexes 2.35-2.48), titan yellow (refractive indexes 2.6-2.9), Strontium yellow (SrCrO4, refractive index 1.9), a chrome oxide (refractive index 2.5), Inorganic pigments, such as a cobalt blue (CoO-nAl 2O3, refractive index 1.7), cobalt purple [Co3 2 (PO4) and refractive indexes 1.67-1.79], and manganese purple [(NH4) 2Mn (P2O7)2 and refractive indexes 1.67-1.72], can be mentioned. Moreover, two or more sorts of mixture of these non-subtlety particles can also be used.
[0018] Carbon black, acetylene black, graphite, etc. can be illustrated as black pigment made to coexist with an un-black non-subtlety particle. Moreover, a with an aforementioned refractive indexes of 1.5 or more black non-subtlety particle can also be used as black pigment. The degree of black of the paint for internal reflection prevention can change with uses, therefore can also change the addition of black pigment by the use. However, it is appropriate to make it the optical density of the paint which generally contains an un-black non-subtlety particle and black pigment become one or more.
[0019] the optics which prepares the refractive index of an internal reflection prevention film and this internal reflection prevention film with which the addition to the paint of the black non-subtlety particle whose refractive index is 1.5 or more, or an un-black non-subtlety particle is obtained using this paint -- obtain for a difference with the refractive index of a member to become less than 0.1 -- preparing is desirable The difference of the refractive index of an internal reflection prevention film and the refractive index of the optical faculty material which prepares this internal reflection prevention film is 0.05 or less more preferably. It is because total reflection in both interface can be extremely lessened by

making small an internal reflection prevention film and an optical faculty material refractive-index difference. In addition, as for the refractive index of an internal reflection prevention film, measuring by the ellipsomter is optimal.

[0020] As mentioned above, the addition of a black non-subtlety particle or an un-black non-subtlety particle is determined by the relation between the refractive index of optical faculty material, and the refractive index of the aforementioned internal reflection prevention film to be used. However, it is appropriate to make the addition into 10 to 60% of the weight of the range to the solid content of the paint for internal reflection prevention. It is because it is not easy to gather the refractive index of an internal reflection prevention film although an addition is based also on the refractive index of PIHIKURU used for a paint at less than 10 % of the weight. It is because there is an inclination for the paint film intensity of the internal reflection prevention film for which the fluidity of the paint for internal reflection prevention stopped being able to apply easily bad and which it formed using this paint to become weak, on the other hand when an addition exceeds 60 % of the weight.

[0021] The paint for internal reflection prevention of this invention contains a vehicle in addition to the aforementioned black non-subtlety particle or an un-black non-subtlety particle. If it is the resin which has resistance in the isopropyl alcohol used for washing of optical faculty material as a vehicle, there will be especially no limit. For example, vehicles for paints generally known, such as mixture of acrylic resin, an epoxy resin, melamine resin, polyester resin, polyamide resin, polyimide resin, or these resins, are used. Furthermore, the paint for internal reflection prevention of this invention can also contain the well-known additive for [, such as a distributed assistant,] paints as occasion demands including a solvent further.

[0022] In this invention, the optical member which has the internal reflection prevention film formed using the above-mentioned paint is also offered. the un-black non-subtlety particle and black pigment whose refractive index the aforementioned internal reflection prevention film contains the black non-subtlety particle whose refractive index a particle diameter is 0.1 micrometers or less, and is 1.5 or more, a particle diameter is 0.1 micrometers or less, and is 1.5 or more -- containing -- and the refractive index of the aforementioned internal reflection prevention film -- the aforementioned optics -- they are the refractive index of a member, and 0.1 or less difference About the un-black non-subtlety particle and black pigment whose refractive index a particle diameter is 0.1 micrometers or less, the black non-subtlety particle and particle diameter whose refractive index is 1.5 or more are 0.1 micrometers or less, and is 1.5 or more, it is the same as that of the above. Furthermore, in the optical member of this invention, total reflection in the interface of an internal reflection prevention film and an optical member can be lessened by making the difference of the refractive index of an internal reflection prevention film, and the refractive index of optical faculty material or less into 0.1. The difference of the refractive index of an internal reflection prevention film and the refractive index of optical faculty material is 0.05 or less more preferably.

[0023] As mentioned above, the addition of the black non-subtlety particle to the inside of an internal reflection prevention film or an un-black non-subtlety particle is determined by the relation between the refractive index of optical faculty material, and the refractive index of the aforementioned internal reflection prevention film. However, it is appropriate to make it 10 to 60% of the weight of the range to an internal reflection prevention film. It is because it is not easy for an addition to cover the expenses [% of the weight / less than 10] of the refractive index of an internal reflection prevention film. It is because there is an inclination for the paint film intensity of an internal reflection prevention film to become weak, on the other hand when an addition exceeds 60 % of the weight.

[0024] An internal reflection prevention film is prepared in the side, periphery side, or KOBA side of optical faculty material, such as a lens and prism. It is suitable that it is the range of about 10-1000 micrometers from a viewpoint of the thickness of an internal reflection prevention film. Application dryness is carried out by the conventional method, and formation of an internal reflection prevention film performs the paint for internal reflection prevention. It has resistance the internal reflection prevention film formed using the paint for internal reflection prevention of this invention has little total reflection in an interface with an optical member, and sufficient also for the isopropyl alcohol used for

washing of optical faculty material.
[0025]
[Example] Below, an example explains this invention further at a detail.
The styrene-monomer 20 weight section, the hydroxy methacrylate 5 weight section, the peroxidation lauryl 0.15 weight section, and the methyl ketone 75 weight section were added to the diameter separable flask of four which attached the manufacture nitrogen introduction pipe of an example 1 (1) vehicle, the polymerization was performed at 80 degrees C under nitrogen atmosphere for 8 hours, and the methyl-ethyl-ketone solution of a vehicle was obtained.
[0026] (2) In the 100g of the manufacture above-mentioned vehicle solutions of the paint for internal reflection prevention, the mean particle diameter measured with laser dispersion type particle-size-analysis equipment added 10g [of aluminum-oxide particles], and carbon black 1g which is 0.07 micrometers, added melamine-ized styrene 10g as a cross linking agent after distribution by the sand mill in them, and prepared the paint for internal reflection prevention in them. After applying the obtained paint for internal reflection prevention to the optical-glass periphery section, heat hardening was carried out for 1 hour, and 130 degrees C of optical members which have an internal reflection prevention film were obtained. Moreover, the refractive index of an internal reflection prevention film was 1.62 as a result of measuring by the ellipsomter. Optical density was 1.6.
[0027] The paint for internal reflection prevention was similarly obtained except changing 10g of aluminum-oxide particles of example 2 example 1 into 5g of zirconium-oxide particles whose mean particle diameter measured with the scanning electron microscope is 0.02 micrometers. After applying the obtained paint for internal reflection prevention to the optical-glass periphery section, heat hardening was carried out for 1 hour, and 130 degrees C of optical members which have an internal reflection prevention film were obtained. The refractive index of inside ********** was 1.67 as a result of measuring by the ellipsomter. Optical density was 2.6.
[0028] In 100g of vehicle solutions prepared in the example 3 example 1, the mean particle diameter measured with the scanning electron microscope added the carbonization silicon particle which is 0.01 micrometers, added melamine-ized styrene 10g after distribution by the sand mill in them, and prepared the paint for internal reflection prevention in them. After applying the obtained paint for internal reflection prevention to the optical-glass periphery section, heat hardening was carried out for 1 hour, and 180 degrees C of optical members which have an internal reflection prevention film were obtained. The refractive index of an internal reflection prevention film was 1.70 as a result of measuring by the ellipsomter. Optical density was 3.0 or more.
[0029] The paint for internal reflection prevention made the same was obtained except changing the aluminum-oxide particle of example 4 example 1 into the titanium black (tradename by MITSUBISHI MATERIALS CORP. "10S") whose mean particle diameter is 25nm. After applying the obtained paint for internal reflection prevention to the optical-glass periphery section, heat hardening was carried out for 1 hour, and 130 degrees C of optical members which have an internal reflection prevention film were obtained. The refractive index of an internal reflection prevention film was 1.70 as a result of measuring by the ellipsomter. Optical density was 3.0 or more.
[0030] In 100g of vehicle solutions prepared in the example of comparison 1 example 1, it added carbon black 2g, melamine-ized styrene 10g was added after distribution by the sand mill in them, and the paint for internal reflection prevention was prepared in them.
[0031] The paint for internal reflection prevention was similarly obtained except having changed the aluminum-oxide particle whose mean particle diameter of example of comparison 2 example 1 is 0.07 micrometers into the aluminum-oxide particle whose mean particle diameter is 0.45 micrometers.
[0032] In 100g of vehicle solutions prepared in the example of comparison 3 example 1, it added coal tar 10g, melamine-ized styrene 10g was added after distribution by ultrasonic gay JINASHIZA in them, and the paint for internal reflection prevention was prepared in them.
[0033] The paint for internal reflection prevention obtained in the evaluation examination 1 example 1 was applied to the base a as for which the right-angled triangular prism 40 (refer to drawing 3) of the ** material FD 2 (the Hoya [Corp.] Corp. make, refractive index 1.652) carried out the rough grind. The

transmitted light 09 which irradiates light 07 from the prism side b as shown in drawing 3 , and is penetrated from the prism side c by this right-angled triangular prism 40 was measured. Intensity of the transmitted light which applied each paint for internal reflection prevention when setting intensity of the transmitted light before applying the paint for internal reflection prevention to 100 was made into the reflection factor, and the value was shown in Table 1. A reflection factor is similarly computed about the paint for internal reflection prevention and the paint for internal reflection prevention of the examples 1-3 of comparison which were obtained from the example 2 in the example 4, and it is shown in Table 1.
[0034] The reflection factor obtained like the evaluation examination 1 was shown in Table 1 except having used the ** material FD 4 (the Hoya [Corp.] Corp. make, refractive index 1.761) as evaluation examination 2 right-angled triangular prism.
[0035] About the sample obtained by the evaluation examination 3 above-mentioned evaluation examination 1, the appearance change after 30-minute washing was observed with the steam of isopropyl alcohol with the naked eye, and the result was shown in Table 1.
[0036]
[Table 1]

各内面反射防止用塗料塗布プリズムの反射率

塗料	反射率 硝材FD2 (1.652)	硝材FD4 (1.761)	イソプロピルアルコール蒸気での洗浄後の外観変化
実施例 1	1.62	9.3	21.5 変化なし
実施例 2	1.67	2.7	13.1 変化なし
実施例 3	1.70	3.4	6.4 変化なし
実施例 4	1.70	2.4	4.2 変化なし
比較例 1	1.53	20.4	36.7 変化なし
比較例 2	1.58	12.6	27.7 変化なし
比較例 3	1.64	6.7	18.8 表面白化、イソプロピルアルコール洗浄液が褐色に変化

[0037]
[Effect of the Invention] The optical member which has the internal reflection prevention film formed using the paint for internal reflection prevention by this invention has little total reflection in the interface of an internal reflection prevention film and an optical member, and there is resistance of enough also in the isopropyl alcohol used for washing of optical faculty material, and it is extremely excellent in practicality. .

[Translation done.]